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EFFECTS OF FRACTURE FLUIDS
ON DEVONIAN SHALES

By

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ABSTRACT

The gas resource locked in the thick hydrocarbon-bearing Devonian shales which underlie much of the Eastern U.S. has been estimated to be up to three times the current proven gas reserves of this country. However, the economic feasibility of producing large quantities of gas from this resource remains in question due to the dense structure and low permeability of these shales. Hydraulic fracturing which usually must be employed to stimulate the gas flow involves significant risk of formation damage by the fracture fluids and resultant plugging of gas-flow channels. Thus, basic investigation of the effects of such fluids on the shale structure and properties, having the objective of developing fracture procedures and technology that will avoid the detrimental damage, is needed.

This paper describes the methods and presents initial results of a current laboratory investigation of the effects of various fluids such as liquid carbon dioxide, aqueous carbon dioxide, water and proprietary fluids on shale under simulated down-hole conditions. The effects are evaluated by in situ measurements of permeability, before and after treatment with the fluid, under various applied pressures and pressure differentials. The nature and extent of the "skin effect" are evaluated by examination of the microstructure of the shale.

It is expected that the results will provide additional insight into the mechanisms of formation damage and will provide guidance to the design and utilization of commercial fracture technology.

INTRODUCTION

The thick hydrocarbon-bearing Upper Devonian Shales, commonly referred to simply as Devonian shale, which underlie many of the Midwestern states has become a primary target for development based on estimates that the gas locked in these shales exceed by several times our current proven reserves. Unfortunately, these shales, formed from muds deposited approximately 350 million years ago are extremely fine grained with very low permeabilities making it difficult to economically produce large quantities of gas from them. The problem is that the system of natural open fractures in the Devonian shale is not particularly extensive nor well interconnected as evidenced by comparison of the low gas flow rates to the gas content present based on the analysis of cored specimens. Thus, well stimulation in the form of fracturing to increase the producing shale surface frequently is necessary to bring the rate of production up.

Among the fracture methods available, hydraulic fracturing currently is employed most frequently. The use of fracture fluids has, however, been found to carry with it the risk of formation damage and a resultant decrease of, rather than stimulation of, gas production.

This paper presents some initial results of a basic investigation of the effect of fracture fluids on Devonian shale structure and properties which is being supported by the Gas Research Institute for the purpose of developing understanding of, and ultimately the capability to avoid, formation damage phenomena.

BACKGROUND DISCUSSION

Formation damage, essentially plugging or blockage of the pore channels of the formation, results basically from plugging or blockage of the pore channels by foreign, induced, or inherent particles, or by very viscous emulsions or fluids. Contact (by infusion) with foreign fluids can result in the formation and/or movement of particles within the pore channel structure of the formation and thus produce plugging and reduction of permeability. The foreign fluids of concern include:

- Drilling fluids
- Clean completion or workover fluids
- Stimulation or well-treating fluids
- The reservoir fluid itself, if modified.

These fluids can produce free-to-move particles or alter pore-channel size in a number of ways including:

- Hydration of swellable clay minerals
- Dehydration of swellable clay minerals
- Dispersion or flocculation of clay minerals and other formation particles
- Dissolution of formation cementing materials (thus freeing particles of other phases)
- Precipitation of salts
- Formation of viscous emulsions.

Montmorillonite is a water-swelling clay mineral which is expanded by adsorbing ordered water layers between crystals. Kaolinite, chlorite and illite are classed as nonswelling clay minerals. However, illite which is a constituent of the Devonian shales becomes a water-swelling material if the potassium ions that bind successive illite crystal units together are

leached out. Mixed clay minerals that contain montmorillonite may expand and degrade, with particles sloughing off, when water affects the inter-lamellar bonding of the montmorillonite. Clay minerals also can swell due to cation exchange with the fluids and are dispersed by rising pH. Particles of other phases present in the formation likewise can be freed when soluble cementing materials that hold them in place are dissolved.

Salt particles may be precipitated within the pore channels due to reactions between constituents of the fluids and components of the formation that are soluble to some degree in the fluids. Viscous emulsions also can be formed in the pore channels under certain flow conditions, involving the interactions of several fluid phases. In addition, emulsions that have been introduced in the course of well drilling or treatment operations can be held in stable states.

The plugging of formation pore channels by particles is flow-rate sensitive. At high flow rates, particles (e.g., clay) that may be attached to formation walls are sloughed off and, along with foreign or induced particles migrate rapidly. At constrictions they are jammed into place, bridging and plugging the channels. Bridging can occur across openings with diameters about three times the particle diameter. At low flow rates the particles can bob around at the pore opening until they ultimately pass through.

When particles have been "plated out" on, or been carried into formations forming blockages, they are not entirely removed by backflush because of the tendency for fluid to flow selectively through those channels that are opened initially. Thus, differences between permeabilities measured with opposing directions of flow in backflush tests provide laboratory evidence of particle movement and bridging or plugging within a core specimen.

Acids used in well treatments can release fines that plug the formation, create sludge, corrode steel and tend to promote emulsion formation.

Alcohol which is sometimes used to lower surface tension can cause salt precipitation.

Thus, it can be seen that a number of physical and chemical effects can be involved in formation damage. Adding further to the complexity of the problem is the heterogeneous nature of the shale. Within a single short well-core section may be shale material differing significantly in physical and chemical properties, having been deposited thousands of years apart.

OBJECTIVE OF THE RESEARCH

The objectives of this research were:

- (1) To determine the nature of the physical and chemical effects of fracture fluids on the shale,
- (2) To quantify these physical and chemical effects and relate them to the properties of the shale,
- (3) To identify means of avoiding the formation damage.

These objectives are predicated on consideration of the generally accepted model of gas production which recognizes the fracture network of the formation to be an initial source of readily accessible gas and ultimately the transportation network for gas coming from the matrix rock. Movement of the gas that is trapped in pores, or otherwise contained in the matrix rock, from the rock into the fracture network ultimately is governed by a permeation process where the gas must pass through the surface region. In accord with the model, the productivity of a well in the gas-bearing

Devonian shale can be enhanced or retarded by alteration of the surface area, porosity or permeability of the matrix rock by the action of an intruded fluid.

GENERAL APPROACH

The general approach employed was that of first making selected property-measurements, analyses or observations on specimens cut from core samples from Devonian shale wells. The specimens then were treated by contacting them with fracture or well-completion fluid under conditions similar to those that might be employed in actual hydraulic-fracture stimulation of eastern gas shale wells. Following the treatment, the property-measurements, analyses or observations were made again, if possible, to assess the effects of the treatment.

In conducting the treatments, the following were experimental variables:

- Pressure
- Treatment time
- Temperature
- Hydraulic fluid composition
- Shale.

The following techniques were considered and/or used for evaluation of the effects of the treatments:

- Permeability measurements
- Measurement of dimensional and mass changes
- X-ray diffraction analysis
- X-ray fluorescence analysis
- Scanning electron microscopy

- Chemical analysis
- Ultrasound-propagation measurements
- Observation of changes of strength and integrity
- Porosity measurements
- Surface area measurements.

Among these, permeability measurement has been the primary evaluation procedure used to-date.

In the early part of the program, shale samples from cores characterized on the Eastern Gas Shale Program of DOE were employed. Samples were selected from wells EGSP WV No. 5 (R146), EGSP NY No. 1 (Y-1) and EGSP OH No. 3 (O-3) having wide ranges of gas contents, open porosity and surface area.

Currently, the investigation is being restricted to experiments with shale samples from a Columbia Gas Company well, 20149, drilled on a program with Gas Research Institute cooperative funding.

FLUID-IMMERSION EXPERIMENTS

Experimental Procedures

Early experiments on shale samples from the EGSP wells used specimens which were 0.25-inch thick by one-inch diameter discs. This size was originally selected to permit the use of the specimens in the permeability apparatus and the physical property test rig. The procedure was to cut 0.25-inch thick slices from the core sample perpendicular to the bore axis. A diamond core drill was then used to remove one-inch diameter specimens from the slice. The slices were cut dry and coring was done wet at very low speeds.

Specimens prepared in this manner had their major faces parallel to the bedding planes of the shale. Hence, permeability, which is measured normal to the major faces, was also measured normal to the bedding planes. Permeability measurements were made prior to any treatments. These measurements were made with helium gas at a one atmosphere pressure differential normal to the bedding planes.

Other property measurements such as those of mass, dimensions, sound-transmission velocity and strength also were made prior to treatments.

The specimens were then set in a screen tray and immersed in the selected fluid inside the pressure vessel for treatments under a range of conditions similar to those that might be employed in actual hydrostatic or gas fracture stimulation of eastern gas shale wells.

After treatment, the specimens were removed from the pressure vessel and permeability and other properties were measured again, as a means of evaluating the treatment effects.

Experimental Results and Discussion

In this type of experiment, specimens were treated with supercritical carbon dioxide fluid, aqueous carbon dioxide and water at pressures in the range from ambient to 2000 psig and at temperatures in the range 20 C to 40 C. As a result of the treatments, specimens were observed to gain weight, lose weight, delaminate and fracture. At the extreme, specimens from EGSP Wells OH No. 3 and WV No. 5 were observed to break into small chips when treated with aqueous carbon dioxide.

Water Blockage and Drying Conditions

A matrix of tests was designed to evaluate the degree of potential water blockage (formation damage) and the effect of vacuum drying as opposed to air drying of the shale samples. Table 1 summarizes the results of these tests. As is indicated in the headings of the columns in the table, the shale specimens were dried, treated with fluid under pressure, then were dried again prior to measurement of permeabilities. All of these specimens were from EGSP well New York No. 1 from the core at the 2538 foot depth. The treatment was with the specimens immersed in aqueous CO₂ (CO₂/water = 2.16 by weight) at ~38 C, ~1350 psi for 48 hours. Permeabilities were measured through the one-quarter-inch thick specimens normal to the bedding planes.

It is apparent from results of this work that vacuum drying does not markedly increase the permeability. It appears that the treatments, which are water-based, do not result in appreciable blockage of the permeability paths as evidenced by the samples which were allowed to air dry. Based on this work, we plan to air dry all of the treated samples. It would appear that air drying to a constant relative humidity will come closest to representing the actual situation.

Figure 1 illustrates some of the other reasons we retain reservations about the use of vacuum. As can be seen, the vacuum drying prior to treatment did produce a minor amount of permeability and it would seem that the vacuum dried samples may have been more responsive to the treatment. This figure also illustrates the effect of vacuum drying the samples which were originally air dried after treatment. In the case of

TABLE 1.

COMBINED RESULTS OF FINAL PERMEABILITY (μ d) OF TREATED, DRIED SHALE SPECIMENS

Processing										
Vacuum Dry Treatment(a) Vacuum Dry			Vacuum Dry Treatment(a) Air Dry			Air Dry Treatment(a) Vacuum Dry			Air Dry Treatment(a) Air Dry	
Sample Number	Permeability, μ d	Sample Number	permeability, μ d	Sample Number	Permeability, μ d	Sample Number	Permeability, μ d	Sample Number	Permeability, μ d	
10	130	19	42.4	8	25.8	34	97.3			
13	160	22	229	14	41.6	37	34.9			
15	67.4	30	3.33	4	39.9	16	177			
29	47.4	31	50.7	11	94.8	17	181			
1	52.4	24	10.8	18	109	21	11.6			
33	13.3	32	15.8	20	13.3	28	259			
Average Permeabilities										
	78.4		58.7		54.1		126.8			

(a) Immersed in aqueous CO₂ (CO₂/water = 2.16 by weight) at ~ 38 C, ~ 1350 psi for 48 hours

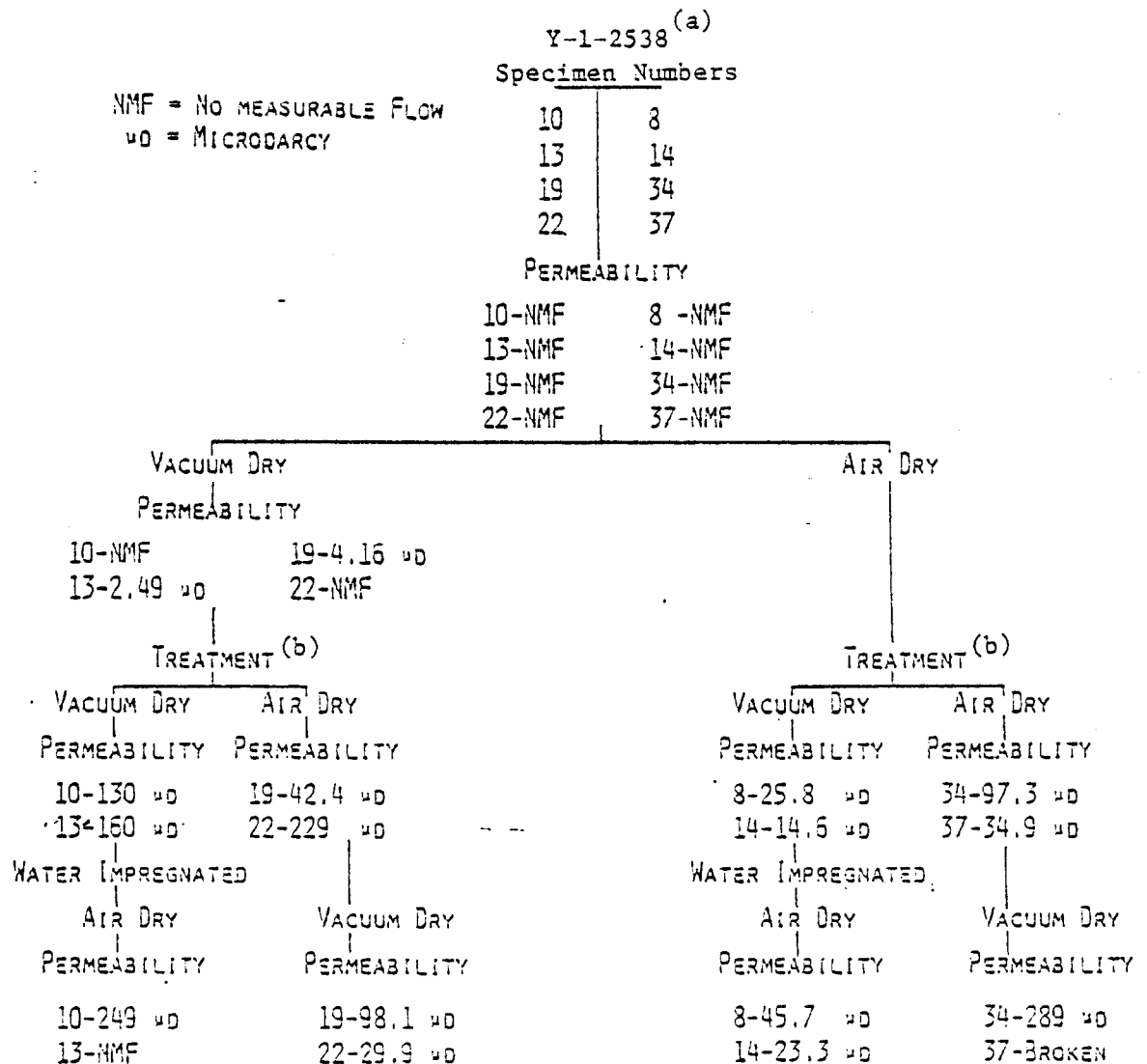


FIGURE 1.

TEST MATRIX TO EVALUATE TREATMENT EFFECTIVENESS AND DRYING CONDITIONS

(a) EGSP Well New York No. 1, 2538 foot core

(b) Specimens immersed in aqueous CO₂ (CO₂/water = 2.16 by weight) at - 38 C, ~ 1750 psi for 48 hours

Sample 22, the permeability decreased dramatically, whereas in the case of Samples 19 and 34, there were permeability increases. It has been postulated that the permeability decrease could have been caused by the collapsing of shale layers due to the vacuum pressure where a carbonate material had been acting as a prop. The permeability increases may be simply due to the removal of additional water. In this experimental sequence we also examined the potential for water blockage in greater detail by reimpregnating the vacuum dried samples and then permitting them to air dry. In three cases the permeability increased and in one case the rather substantial permeability was destroyed. We do not at present have a firm conclusion regarding the reason for this result.

Leaching Experiments

A long-term (eight days) treatment run (Experiment 34836-11) was made with samples from well R-146 with aqueous CO₂ (CO₂/H₂O weight ratio = 2.16) at 40 C, 1300 to 1700 psig. The liquid from this treatment run was evaporated to dryness to recover dissolved solids which were analyzed as a step toward elucidation of the chemical attack. A similar experiment (No. 34836-17) was run using water as the treatment fluid.

Results of optical emission spectographic analysis of the dissolved solids recovered from the two solutions (Table 2) show that the solution in the aqueous CO₂ consisted primarily of calcium and other alkaline earth and iron compounds, whereas the material dissolved by water was mainly alkali metal (Na, K) compounds. A weight of dissolved solids equivalent to 0.32 percent of the weight of the shale treated was recovered from the water while that from the aqueous CO₂ was equivalent to 1.1 percent of the shale weight -- roughly three times the fraction dissolved in

TABLE 2.
CHEMICAL ANALYSIS^(a) OF DISSOLVED SOLIDS

Element	Dissolved in Aqueous CO ₂ (Treatment 34836-11)	Dissolved in Deionized Water (Treatment 34836-17)
	Weight, Percent	Weight, Percent
Ca	Major	2-4
Na	5-10	Major
K	1-3	2-4
Mg	0.5-2	0.1
Sr	0.1	0.03
Ba	0.01	0.1
B	0.1	0.3
Cu	<0.01	<0.01
Ni	6-10 ^(b)	0.1
Si	2-4	3-5
Fe	1-3	0.2
Al	0.5	0.3
Mn	0.2	<0.01
Co	0.02	<0.01
Cr	0.02	0.03
Ti	0.02	<0.01
Mo	-	-

(a) Optical emission spectrographic analysis; other elements were sought, but were not found.

(b) Shown to be from pressure vessel.

water. Results of analysis of the liquid from a blank run (no shale specimen) made with aqueous CO₂ under identical conditions showed the presence of nickel but not iron. Thus, the iron apparently was dissolved from the shale, while the source of the nickel is indicated as a component of the pressure vessel.

Ultrasonic Tests

Ultrasonic transmission velocity measurements, the results of which are given in Table 3, were made with a single set of shale specimens before and after treatment in aqueous CO₂ under pressure. The results show little or no effect in the horizontal direction (i.e., the radial direction of a well-core section). However, in all but one pair of specimens, ultrasonic travel time in the vertical direction is increased significantly. This is interpreted to indicate that voids or separations in the shale have been produced by the treatment. . . .

SIMULATED DOWN-HOLE EXPERIMENTS

Experimental Procedures

The previously described application of hydrostatic pressure to specimens immersed in fluid is not a good simulation of the unidirectional application of fluid pressure outward into the shale from a well bore during fracturing. A preferred way of treating shale with fluid and of simulating the entrance of fluid into the shale formation during fracturing would be to apply pressure unidirectionally. To simulate conditions following a hydraulic fracture, the liquid would be removed and gas pressure would be applied in the opposite direction duplicating the tendency for

TABLE 3.
 RESULTS OF ULTRASONIC VELOCITY TESTS ON SHALE SPECIMENS
 BEFORE AND AFTER TREATMENT
 (Treatment 34836-15, Aqueous CO₂)

Sample Number	Travel Time (Microseconds)				Comments
	Radial Direction		Axial Direction		
	Before	After	Before	After	
R-146-3311-4	6.0	6.0	2.75	5.8	
R-146-3311-3	5.9	5.95	2.95	6.05	
R-146-3311-2	5.85	5.85	2.55	5.5	
R-146-3311-1	6.0	6.0	4.10	6.45	
R-146-3201-3	6.3	6.0	3.8	8.5	Split in half after treatment
R-146-3201-1	6.65	Broken	3.8	Broken	Fell in pieces after treatment
R-146-3341-3	6.3	6.05	3.1	2.7	
R-146-3351-2	6.35	6.2	2.75	2.6	

the gas to flow from the formation. An apparatus has been designed and assembled with which shale specimens can be carried through such a sequence.

Illustrations of the apparatus are shown in Figures 2 and 2a. As indicated, the shale specimen is mounted to permit the unidirectional application of gas or fluid pressure in either direction and the measurement of permeation rates through the shale while maintaining a simulated lithostatic pressure on the specimen. Two methods of permeation measurement can be implemented. The volume of gas flow can be measured with a gas buret if the pressure drop is to atmospheric pressure. At elevated pressures and at various pressure differentials, the rise of pressure in a high-pressure receiver of known volume can be measured by use of a pressure transducer. Although permeabilities usually have been determined using helium, other gases such as carbon dioxide, methane, hydrogen can be employed equally well. Permeabilities determined with carbon dioxide have been found to differ from helium permeabilities by only about ten percent.

Specimen preparation procedure is to cut one-inch thick vertical slices from the core sample parallel to the bore axis. The slices are cut into one-inch cubes which are then sanded into cylinders. The resulting specimens are one-inch thick by one-inch diameter cylinders cut entirely dry with bedding planes running normal to the major faces. Sample holders have been designed in which the sample is mounted with epoxy cement at the top and bottom and a gas impervious sheath surrounds the outer circumference allowing unidirectional flow of fluids or gases through the sample parallel to bedding planes, duplicating the predominant direction of flow of fluid and gas through the shale at the surface of a well bore and of a vertical fracture face. This method of mounting the shale specimen for determination

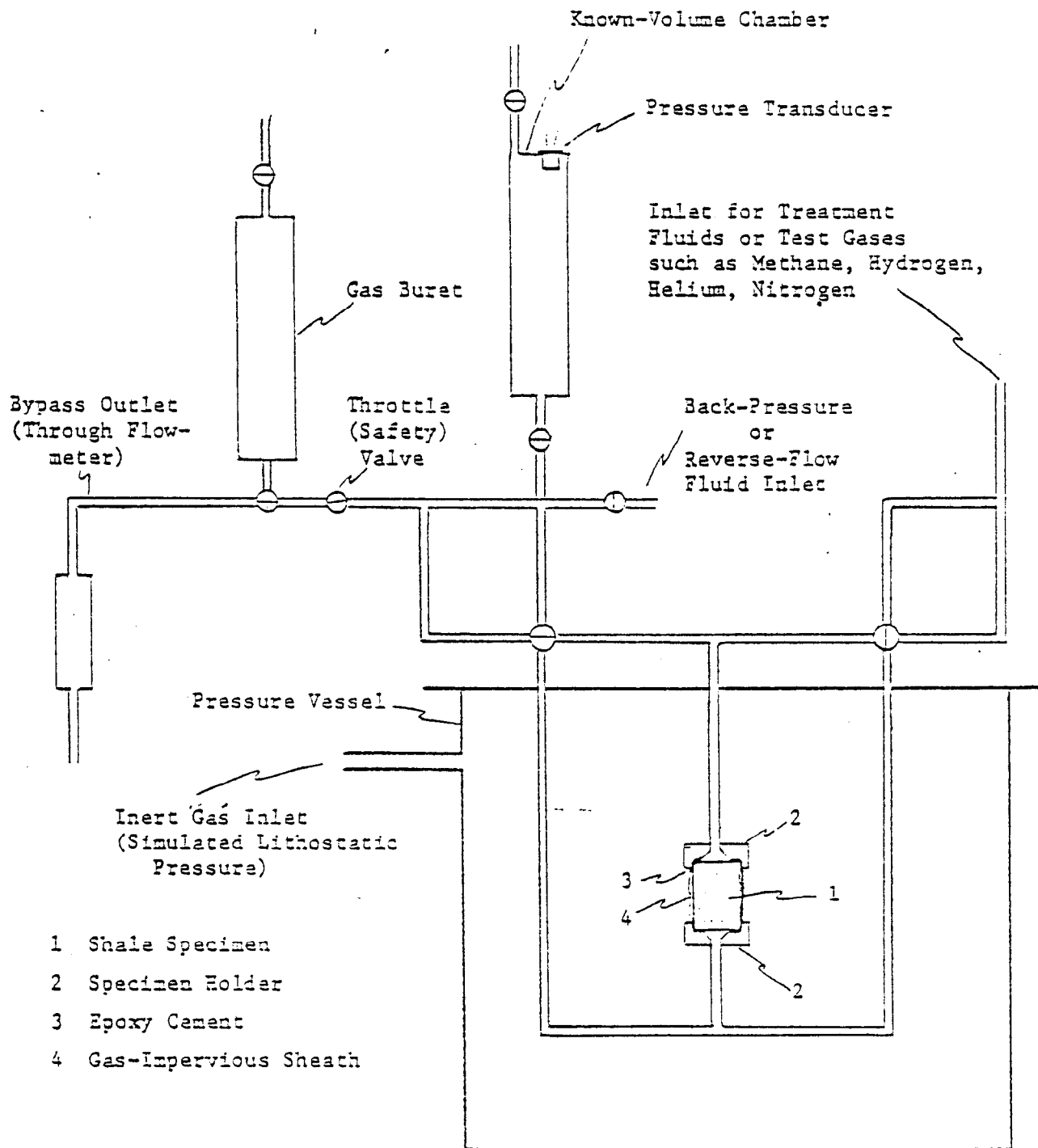


FIGURE 2.

SCHEMATIC OF APPARATUS FOR INVESTIGATION OF THE EFFECTS OF FRACTURE AND TREATMENT FLUIDS ON SHALE UNDER DOWN-HOLE CONDITIONS

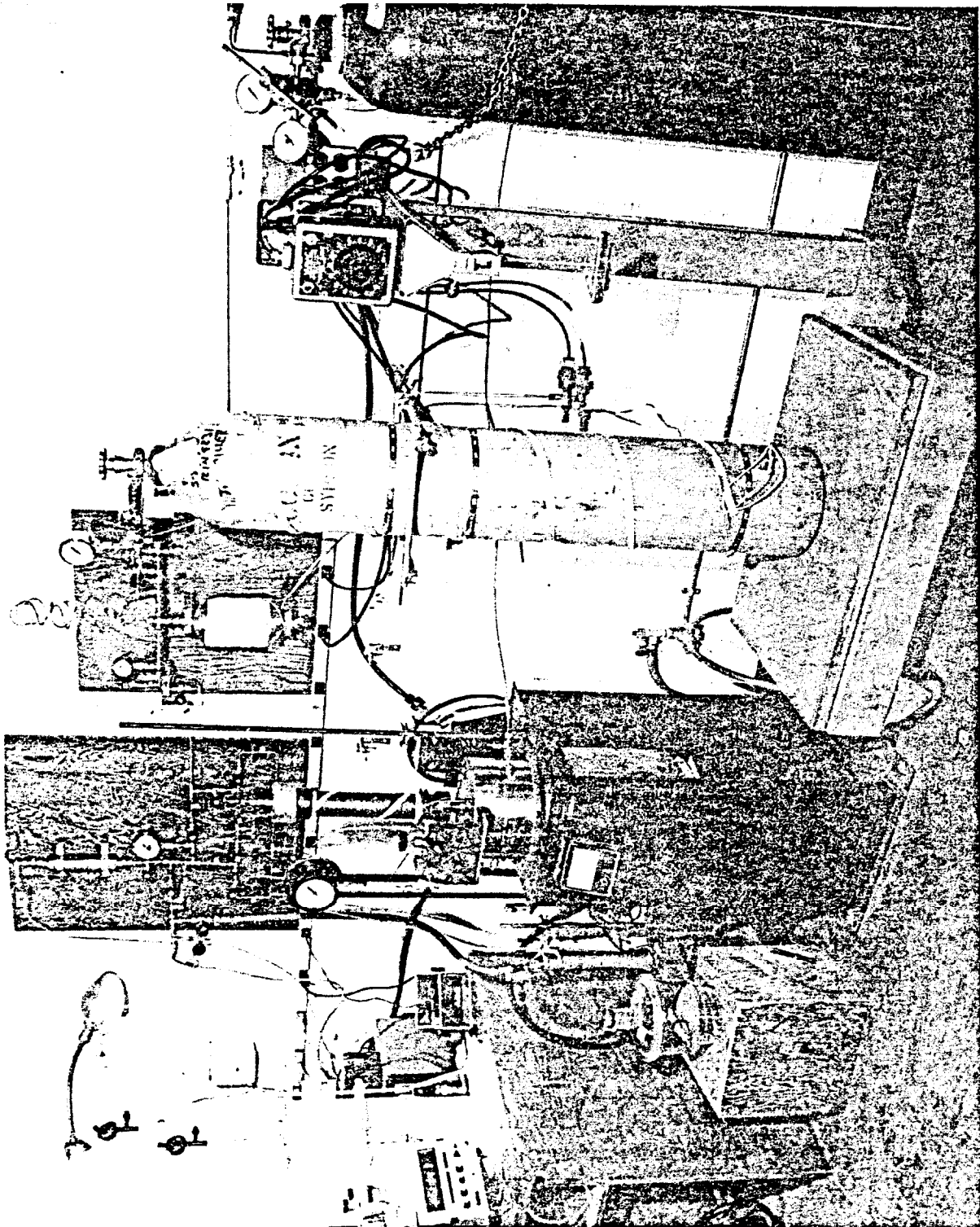


FIGURE 2a. PHOTOGRAPH OF CURRENT APPARATUS SET-UP

of permeability and for the in situ treatments at elevated pressures has been found satisfactory for use at pressures up to at least 1100 psi.

For purposes of recording and reporting data on this work, several conventions have been adopted. One direction of flow through the shale specimen has been designated the forward direction, analagous to the direction gas would flow through the shale when a well is in production. The reverse direction, then, will always be the direction in which the force intended to drive the flow of fracture fluids will be applied. Following the hydraulic fracture fluid treatment, the gas, driven by formation pressure, would tend to flow in the forward direction carrying fluid that had penetrated the shale out with it. Thus, following the laboratory hydraulic fluid treatments, gas pressure was applied in the opposite (forward) direction to monitor the value and/or the recovery of permeability as that process occurs.

A second convention is that of maintaining a constant containment pressure surrounding the shale specimen within the pressure vessel. The containment pressure is held constant at a level corresponding to the estimated lithostatic pressure for that depth from which the well core sample was taken. The maximum applied pressure (i.e., the pressure applied to drive the gas through the shale) is held at 100 psi below the containment pressure.

Currently, all experiments are being conducted at room temperature (17 to 20 C) to insure that some data are obtained.

Specimens are labeled according to well number, core depth and location within the core. Hence, a sample labeled "20149-680.14-a-2" is from well number 20149 at a depth of 680.14 feet. The designation "a-2" refers to the slice of core sample taken and the exact location within

that slice of the specimen. All specimens are stored in dessicators following removal from the sealed cans in which they were delivered to minimize potential deterioration.

The apparatus and the procedures that have been developed are seen to be significant because they make possible:

- The determination of permeabilities at down-hole pressures and ambient conditions
- The determination of permeabilities, treatment and posttreatment redetermination of permeability of a single specimen without disturbing the specimen.

The effect of having down-hole containment pressure is illustrated in Figure 3. It can be seen that the determined permeability varies significantly with containment pressure and that the permeability determined with about 1100 psi simulated lithostatic pressure is quite different from that which would be obtained from measurement at one atmosphere ambient.

Experimental Results and Discussion

Helium permeabilities were determined over a range of applied pressures and with a constant containment pressure simulating the estimated lithostatic pressure for several specimens from Columbia Gas Well 20149 at the 680 foot depth. The results, shown in Figures 4 through 6, indicate that permeabilities are in the range of 20 to about 5000 microdarcies and that they generally increase with increasing applied pressure. This increase is believed due to added permeation through additional (finer) channels as the pressure differential was increased and as the applied pressure approached the containment pressure. The differences between permeabilities determined for the two flow directions are greater than the

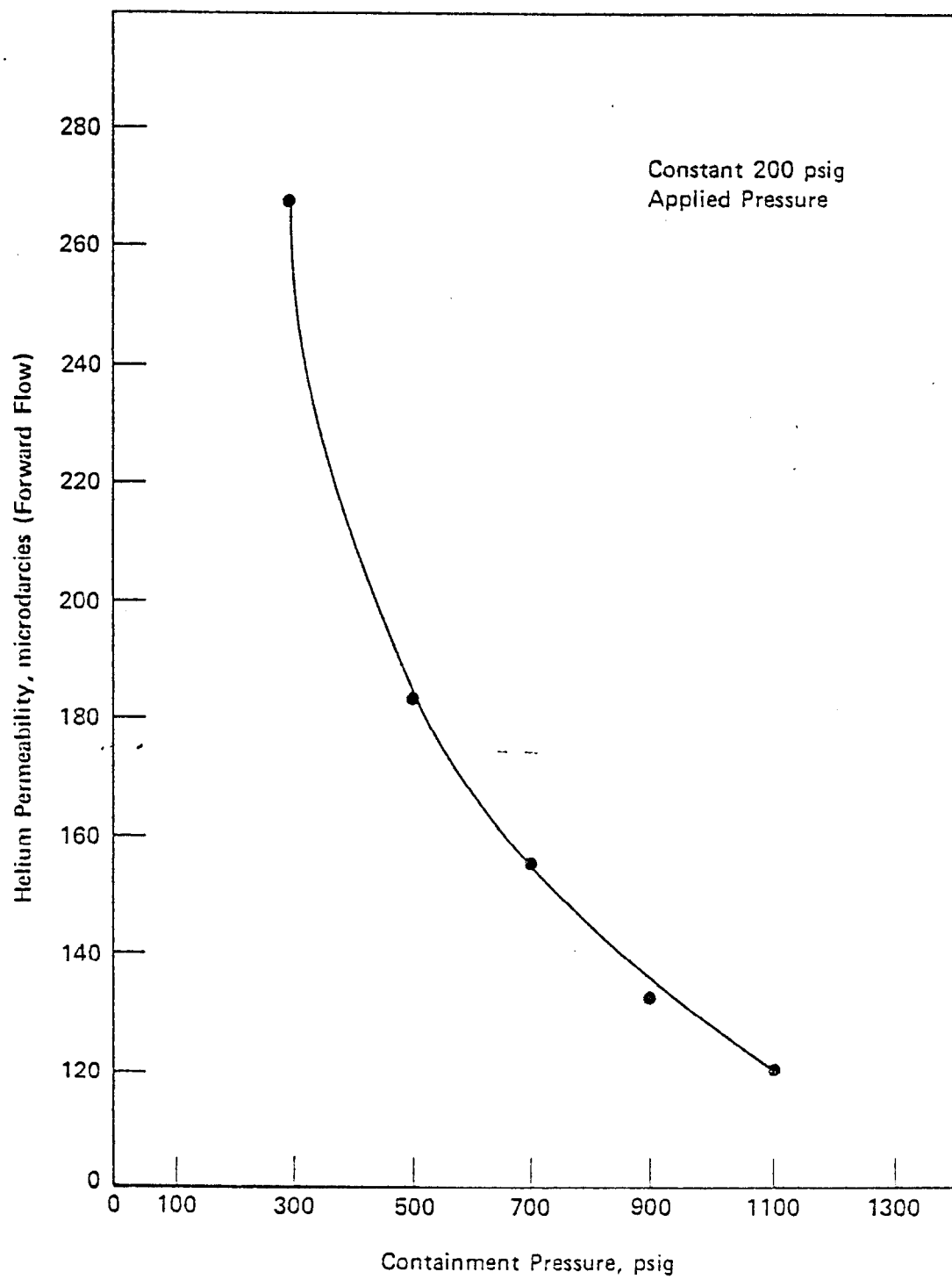


FIGURE 3.
PERMEABILITY VERSUS CONTAINMENT PRESSURE FOR SPECIMEN Oh 3-1015.5-a-3

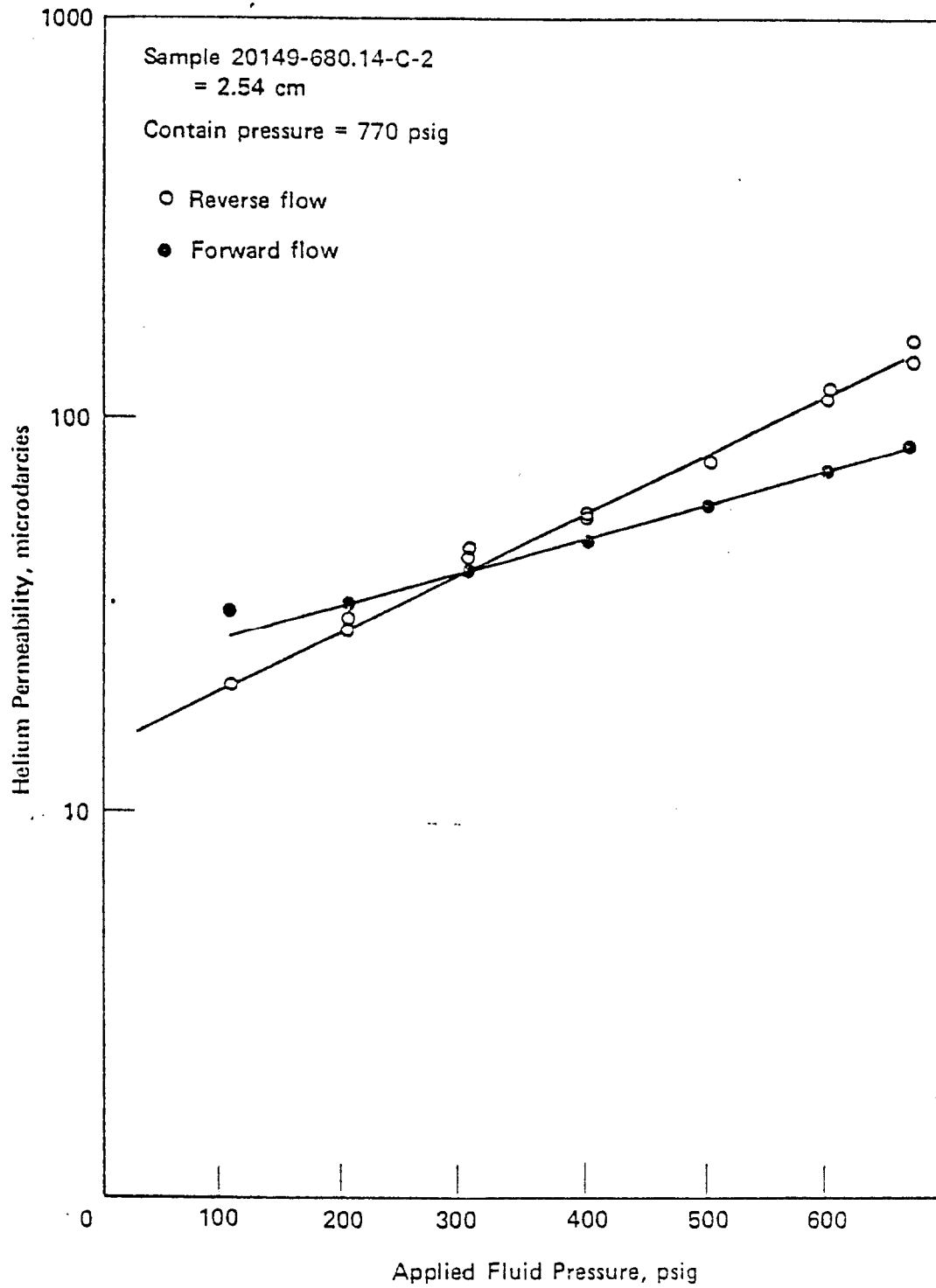


FIGURE 4.
PERMEABILITY DATA FOR SHALE SPECIMEN 20149-680.14-C-2

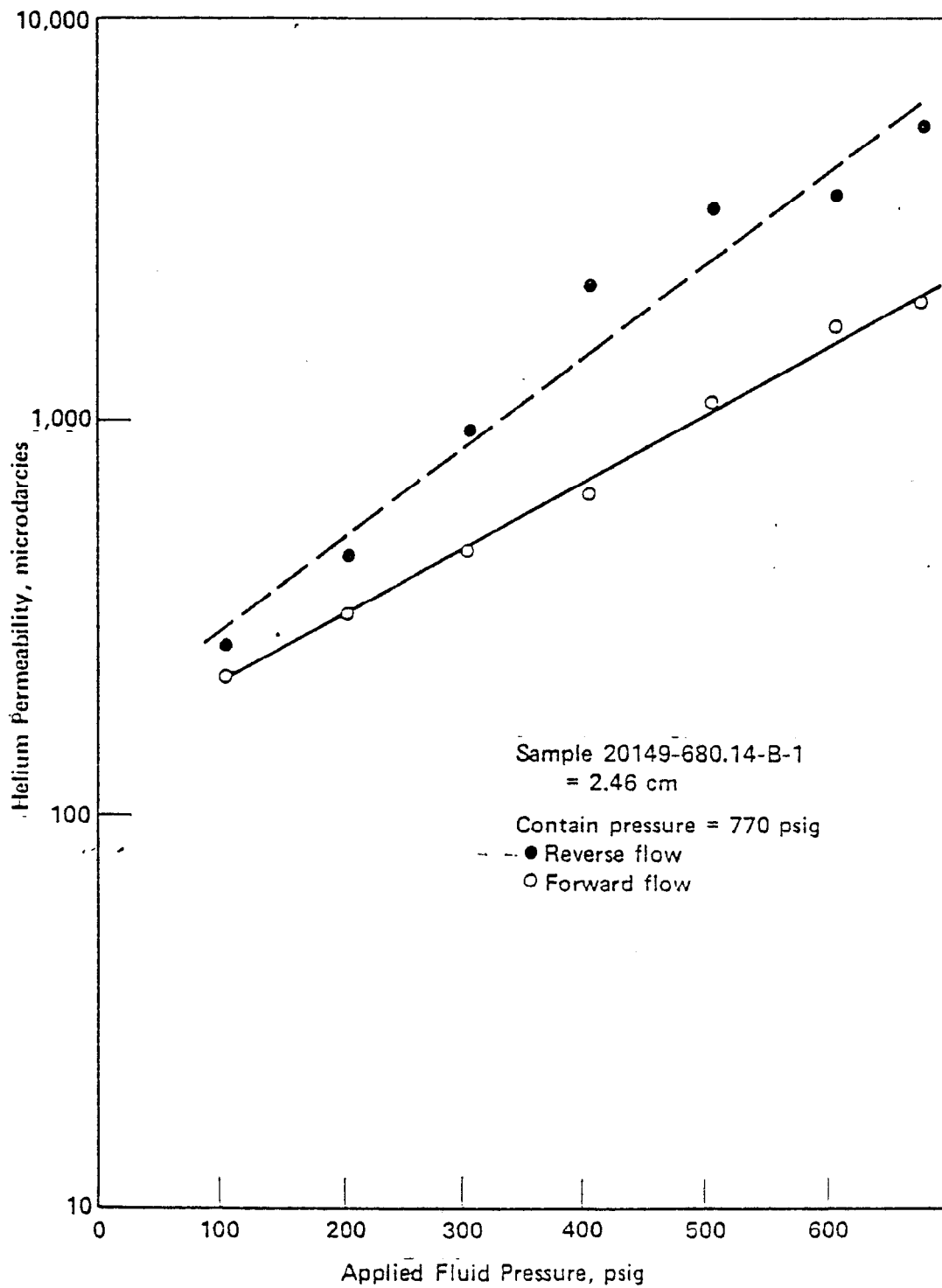


FIGURE 5.

PERMEABILITY DATA FOR SHALE SPECIMEN 20149-680.14-B-1

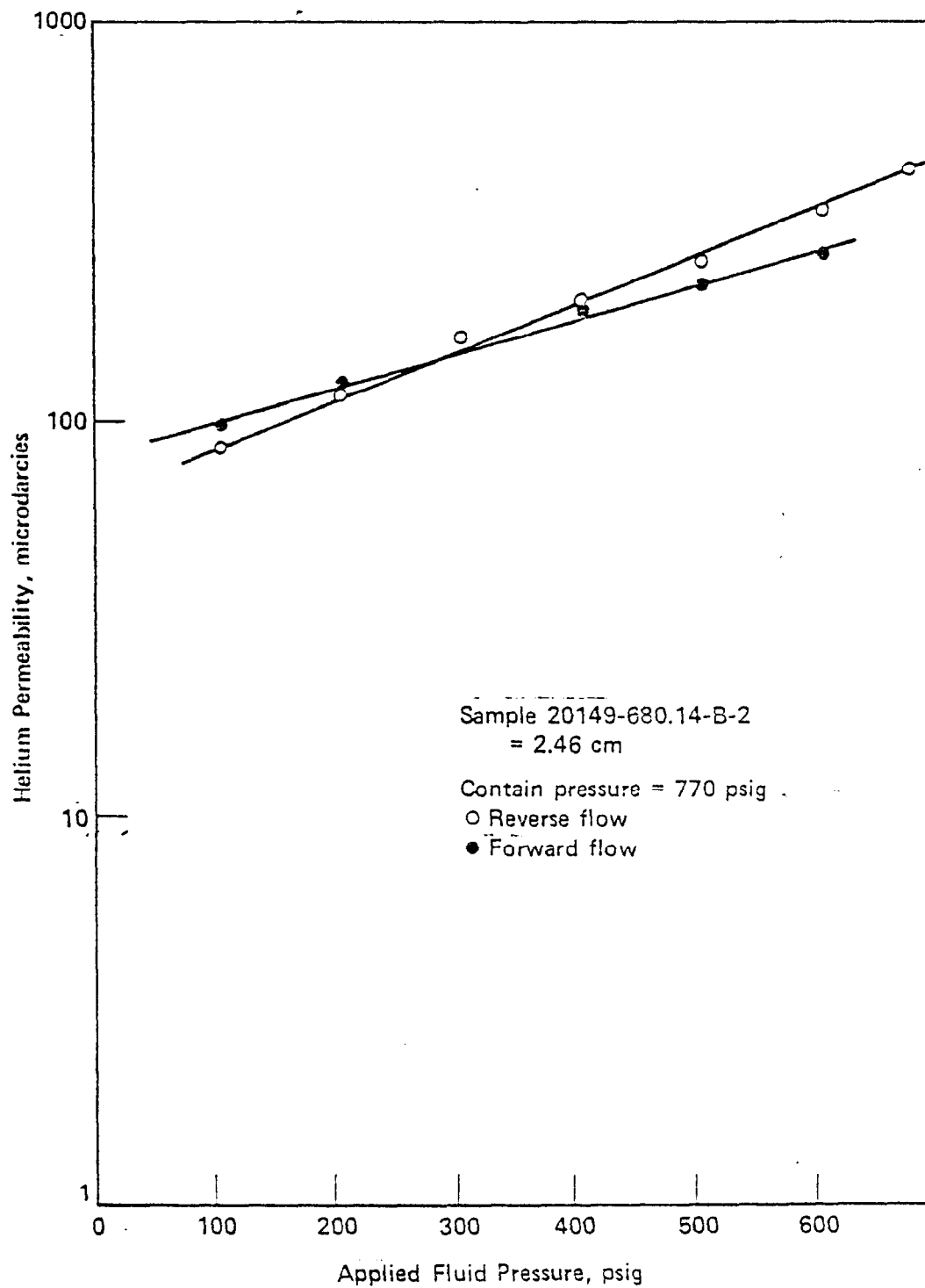


FIGURE 6.
PERMEABILITY DATA FOR SHALE SPECIMEN 20149-680.14-B-2

expected experimental error and therefore are believed to be real. They are believed to be due to the movement of fine particles within the gas-flow channels of the shale or a differential blocking action of particles at the two specimen surfaces. It can be seen that the permeabilities are significantly higher for the B slice than for the adjacent C slice from the core.

A number of shale specimens were treated with fracture fluids, with permeability determinations being made before and after treatment using the scenario that has been described. Short discussions of the experiments follow.

Specimen NY-1-2765. Helium permeability data for one of the New York shale specimens, obtained before and after a five-hour treatment with aqueous CO₂ as is indicated in the figure, are shown in Figure 7. It should be noted that this early experiment differs from the standard procedure with respect to the containment pressure; in this experiment containment pressure was adjusted with applied pressure to a 100 psi higher value. Two sets of permeability determinations were made on different days before the treatment to assess reproducibility. In the first set, duplicate measurements were made and it is believed that the reproducibility of the measurements is well within the difference shown between the two sets of measurements. This sample was kept in tank helium atmosphere in the apparatus in the interim between measurements. The cause of such changes in permeabilities which have been observed for other specimens, are not known with certainty, but are believed to result from changes in humidity and/or pressure the specimens are subjected to during the measurements. The fairly large increase of permeability produced by vacuum drying the sample has been observed for other specimens and is

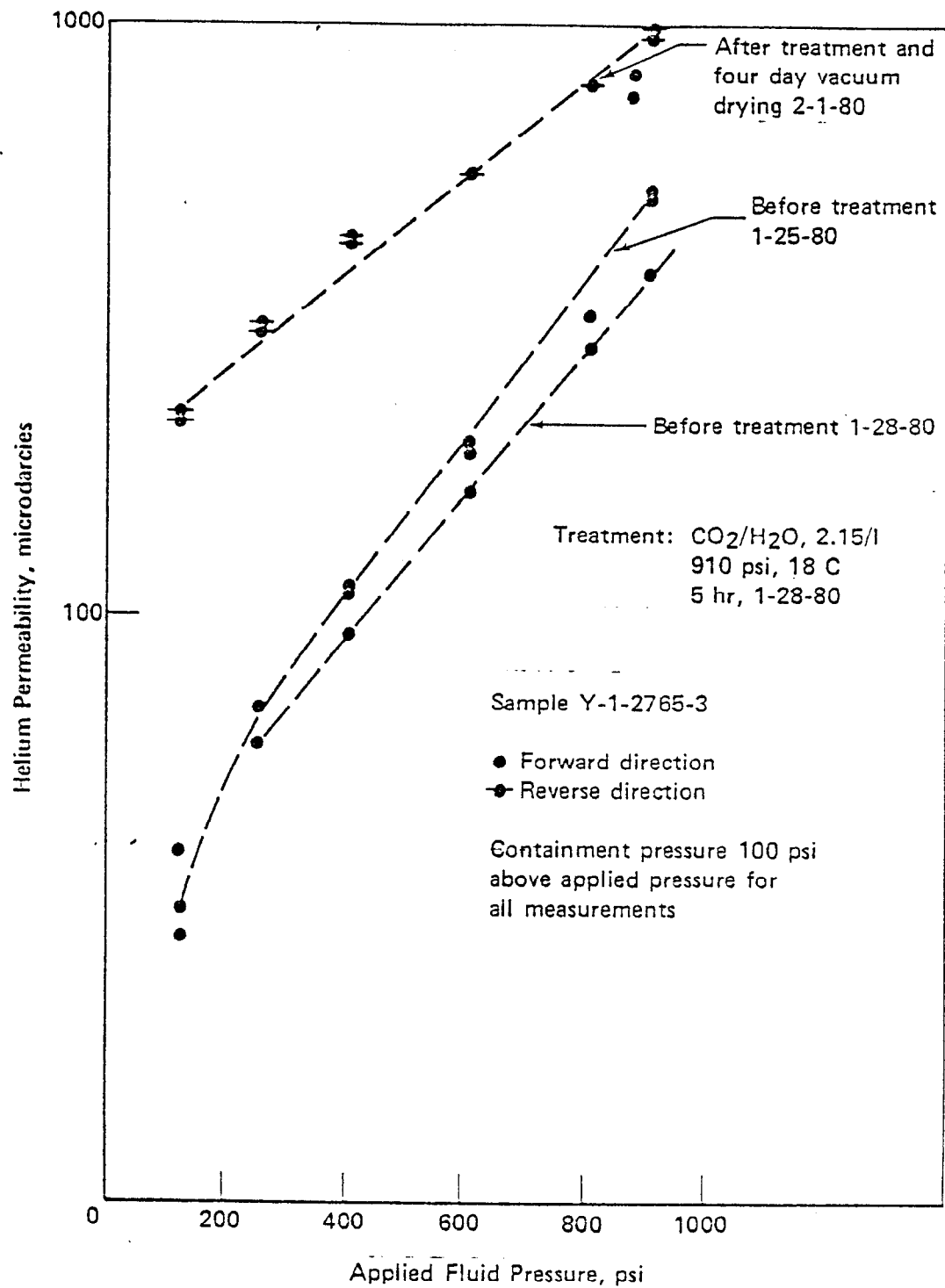


FIGURE 7.
PERMEABILITY DATA FOR SHALE SPECIMEN FROM EGSP
NEW YORK WELL NO. 1, 2765 FOOT DEPTH

believed due to the removal of infused fluid.

Specimen 29149-680.14-a-2. Permeability data for specimen 20149-680.14-a-2 which are presented in Figure 8 show that following the twenty-five minute treatment with 33 percent carbon dioxide in water, the forward flow permeability which dropped from approximately 40 to 14 micro-darcies at 500 psig slowly recovered and in a period of 140 hours (about six days) levelled off near its pretreatment value. The reverse-flow permeability which had initially been much lower than the forward permeability was found to be up near the latter following the short treatment, possibly indicating that some gas-flow inhibiting particulate material was dissolved by the fluid. An additional 25 hours of treatment with the 33 percent aqueous carbon dioxide did not appear to change the reverse flow permeability at 500 psig. No permanent adverse effect of the 33 percent aqueous CO₂ fluid is indicated in these initial results.

Specimen 20149-1030.32-a-2. The ends of this specimen had been polished in preparation for after-treatment microscopic and/or X-ray evaluation of the effects of the treatment. Under applied pressures up to 900 psig, no flow of helium through the specimen could be detected. It was felt that clogging of the pores of the shale produced by the polishing could be blocking the gas-flow channels. To check this, the polished surfaces were scraped, removing the potentially smeared layers. Following this, there still was no detectable flow of helium through the shale under 800 psig of applied pressure.

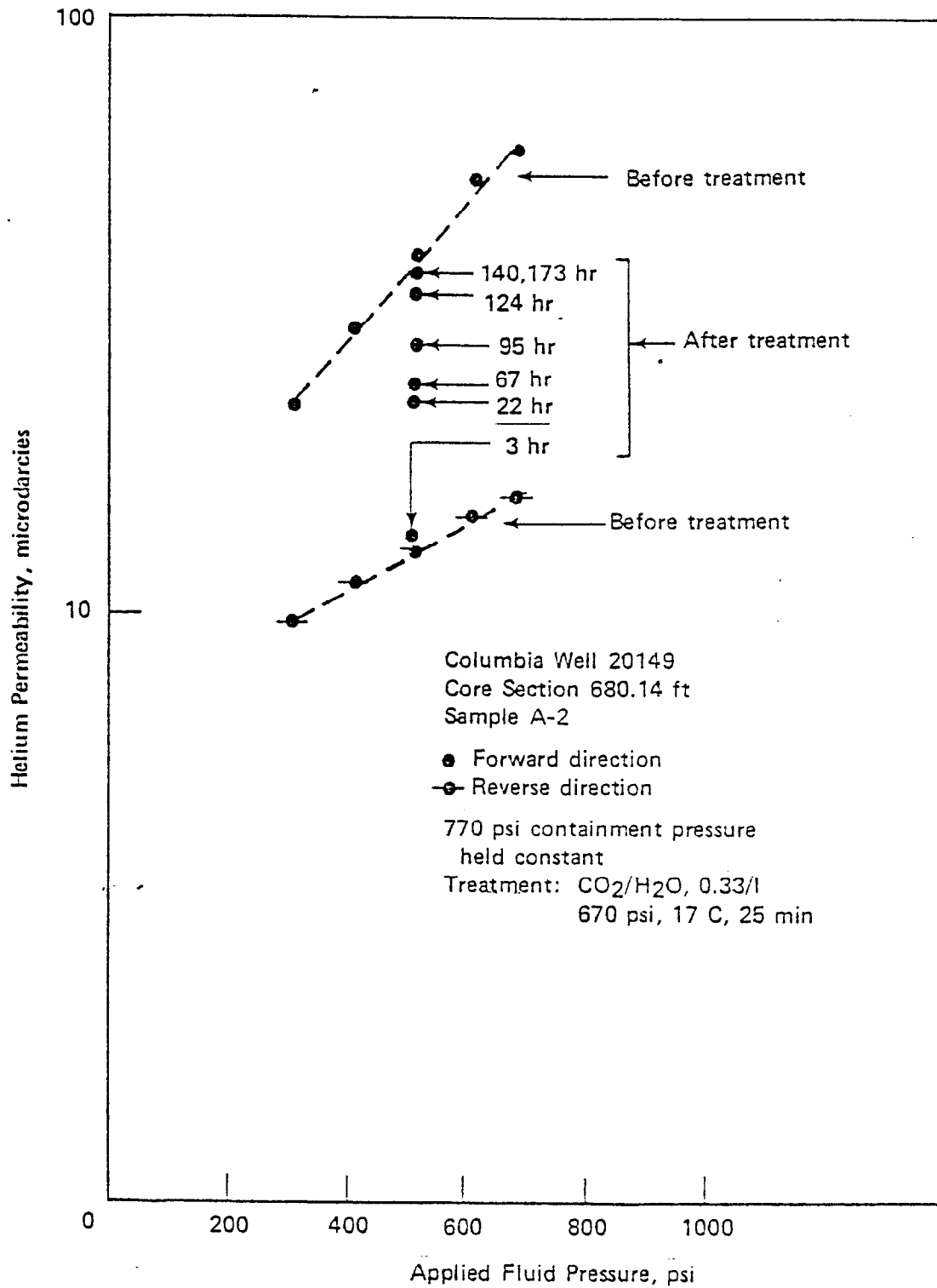


FIGURE 8.
PERMEABILITY DATA FOR SHALE SPECIMEN 20149-680.14-A-2

Specimen 20149-1030.32-a-3. An X-ray diffraction pattern was run on the to-be treated surface of this specimen prior to mounting. The results of permeability determinations before and after treatment with 33 percent aqueous CO₂ at 800 psig for four hours (Figure 9) show that some gas flowed through this specimen. However, the flow rate was reduced by the treatment, and decreased further with time under continuously applied pressure, to a value after 90 hours corresponding to a permeability less than one microdarcy. An "after-treatment" X-ray diffraction pattern is to be run on this specimen.

Specimen 20149-680.14-b-2. Since the first two treatments of specimens from this core with 33 percent aqueous CO₂ for 25 minute and 25 hour periods appeared to have little irreversible effect, the period of treatment of this specimen was extended to 64 hours at 670 psig pressure. The result of permeability determinations which are shown in Figure 10 indicate that the permeability was reduced nearly two orders of magnitude (from ~250 to ~3.3 microdarcies at 500 psig) by the treatment. There appears to be a recovery with time, the permeability has risen only to nine microdarcy after 210+ hours. Permeability may eventually recover to the initial range, but a very long time may be required. The blockage could be due to infused fluid, a reaction between the fluid and the matrix, or both of the two.

Specimen Oh 3-1015.5-a-3. Before treatment, this specimen exhibited permeabilities in the range 30 to 80 microdarcy. As is shown in Figure 11, treatment with water for two hours at 700 psig decreased the determined permeabilities to about six microdarcy, with little or no

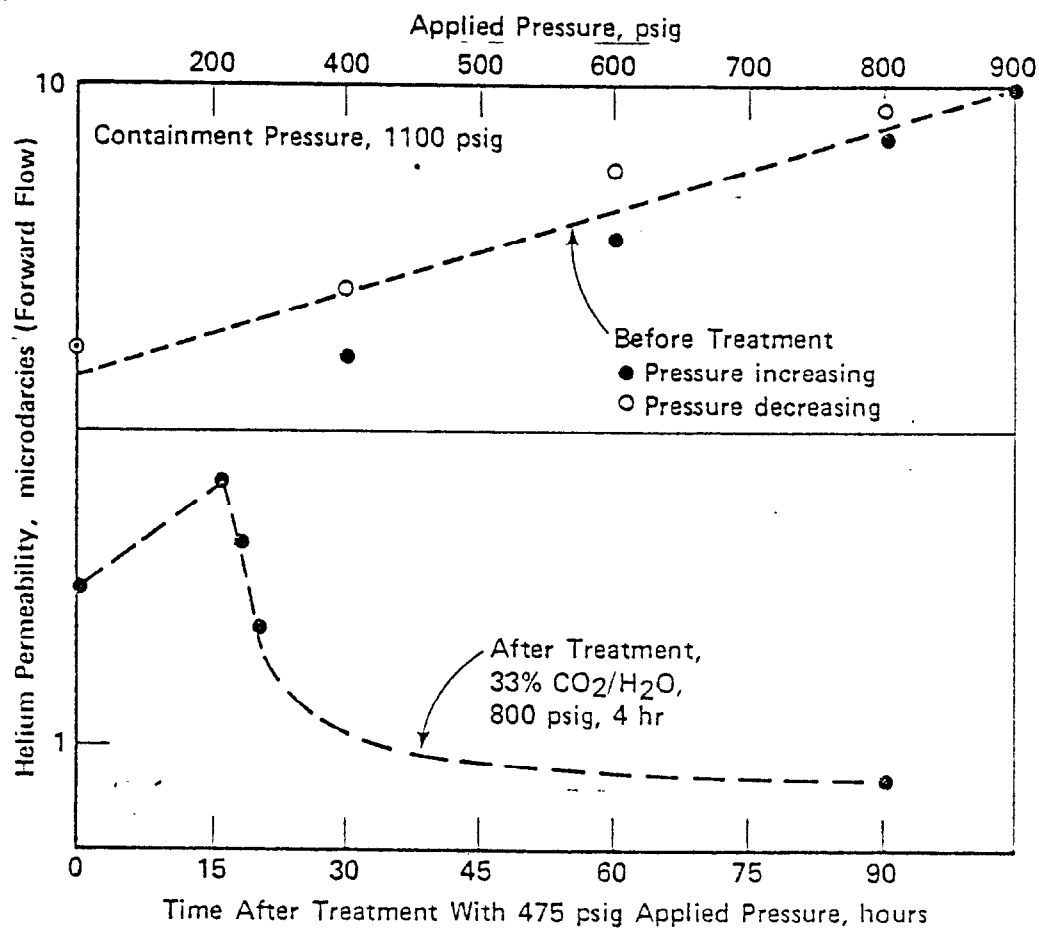


FIGURE 9.
HELIUM PERMEABILITIES FOR SPECIMEN 20149-1030.32-a-3

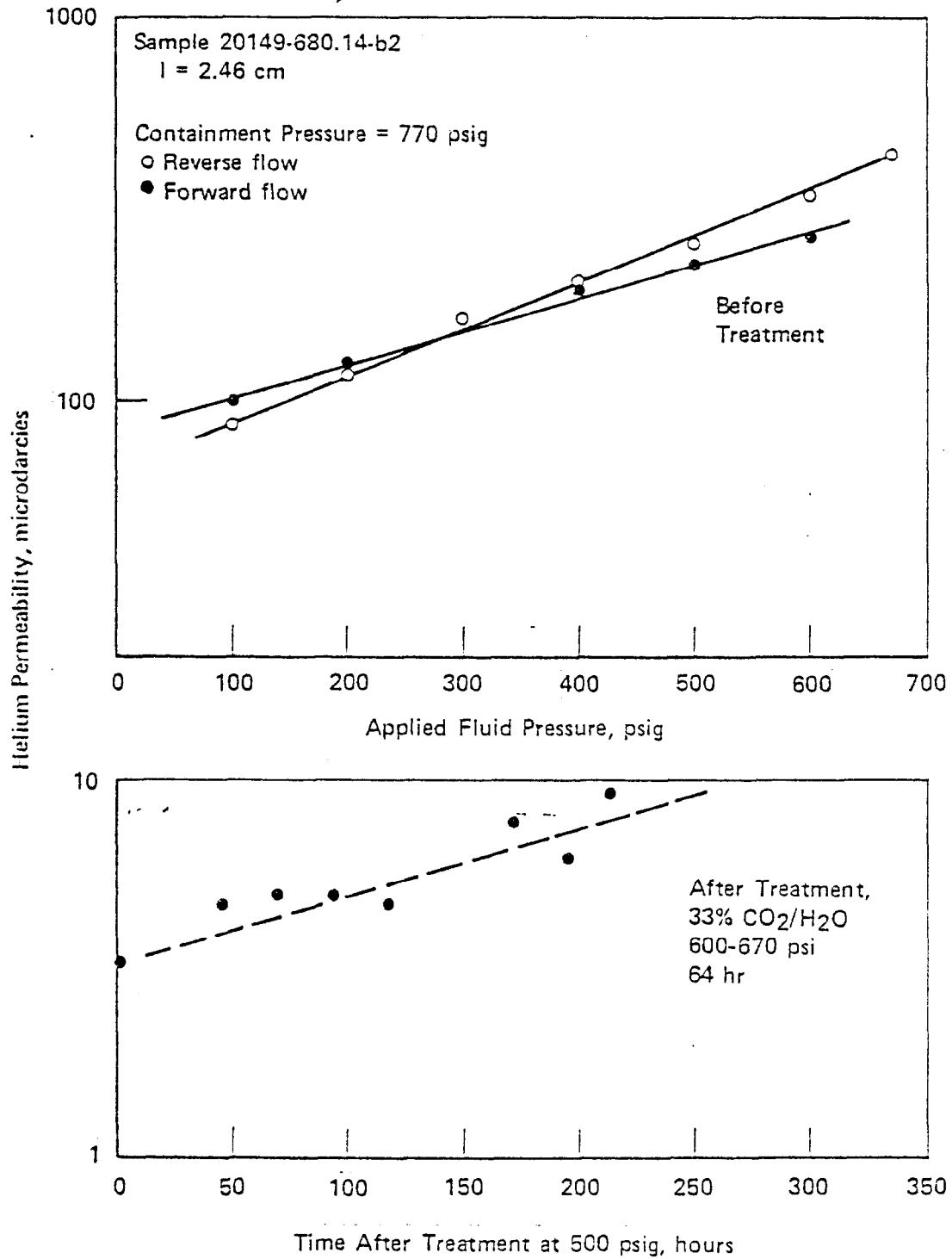


FIGURE 10.
 PERMEABILITY DATA FOR SHALE SPECIMEN 20149-680.14-b-2

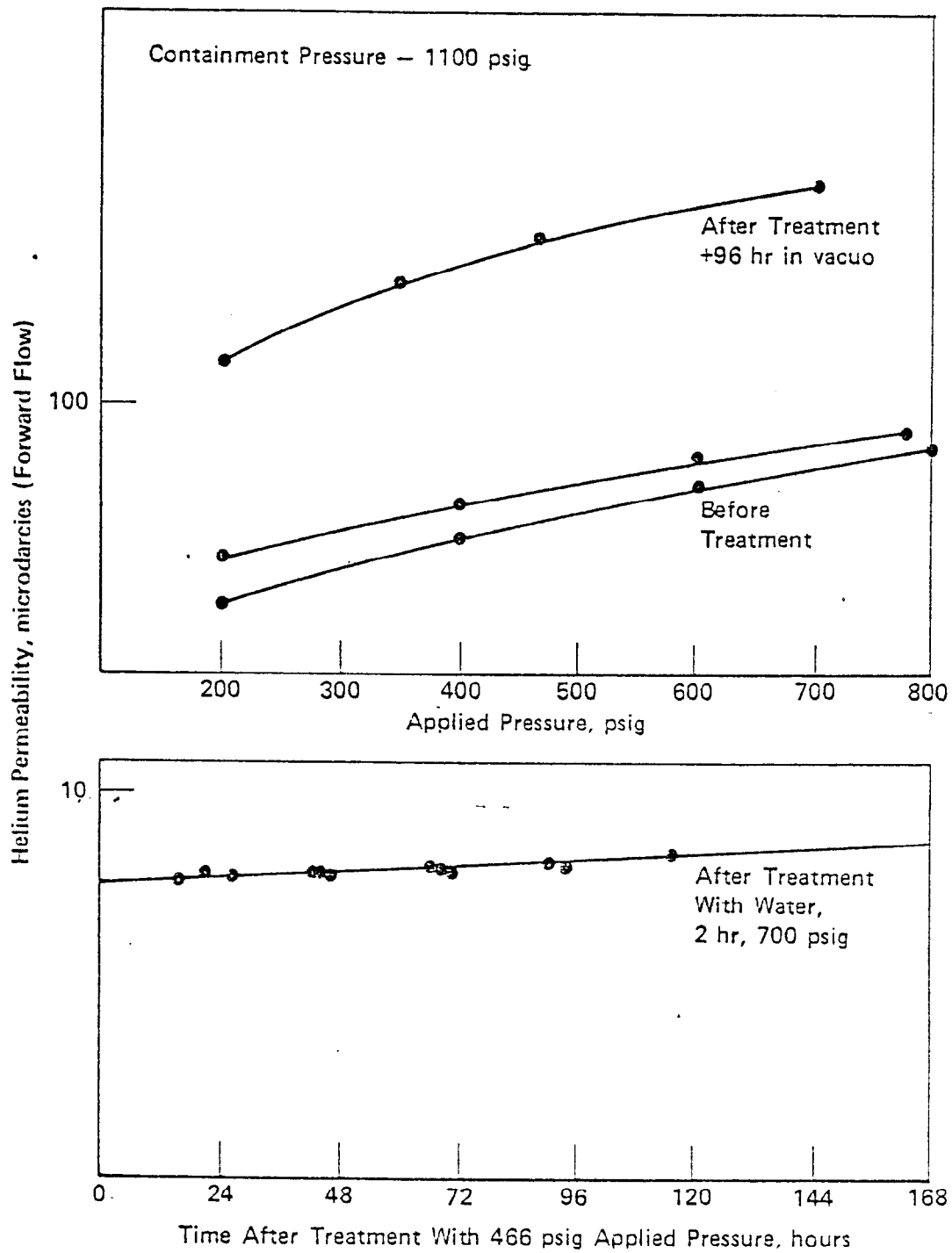


FIGURE 11.
HELIUM PERMEABILITIES FOR SHALE SPECIMEN Oh 3 1015.5-a-3

significant increase after five days under unidirectional applied gas pressure. However, following 96 hours in vacuo, the observed permeabilities were increased to the range 100 to 400 microdarcy. The results suggest that the use of reduced pressure may be one means of clearing liquid blockage and of improving gas permeation rate.

Specimen 20149-1030.32-a-4. The results of determinations of the permeability of this specimen before and after treatment with kerosene which are shown in Figure 12, indicate that the permeability before treatment passed through a minimum as pressure was increased. One possible explanation for the seemingly anomalous variation of permeability with pressure is based on the movement of very small particles within the gas-flow passages of the shale. At low pressures, gas-flow velocities are low and the small particles may be at rest within the void spaces, having little or no effect on gas flow. As pressures and thus velocities are increased, the particles within the voids (i.e., wide portions) of the flow system are picked up and carried to narrow portions of the passages where they lodge, blocking flow either as single particles or as a collection of particles bridging the passageways. As pressure is increased further, additional small passages that have been held essentially closed by the containing pressure or are too small to be effective conductors at low pressures come into play as significant gas-flow passages and observed permeability increases with increasing pressure.

It can be seen in Figure 12 that the permeability in the pressure range of greatest interest initially dropped from about 2.9 microdarcy to zero flow. The flow recovered with time, and, after about 20 hours, appears to have stabilized at about 2.2 to 2.3 microdarcy -- 75 to 80 percent of the before-treatment value.

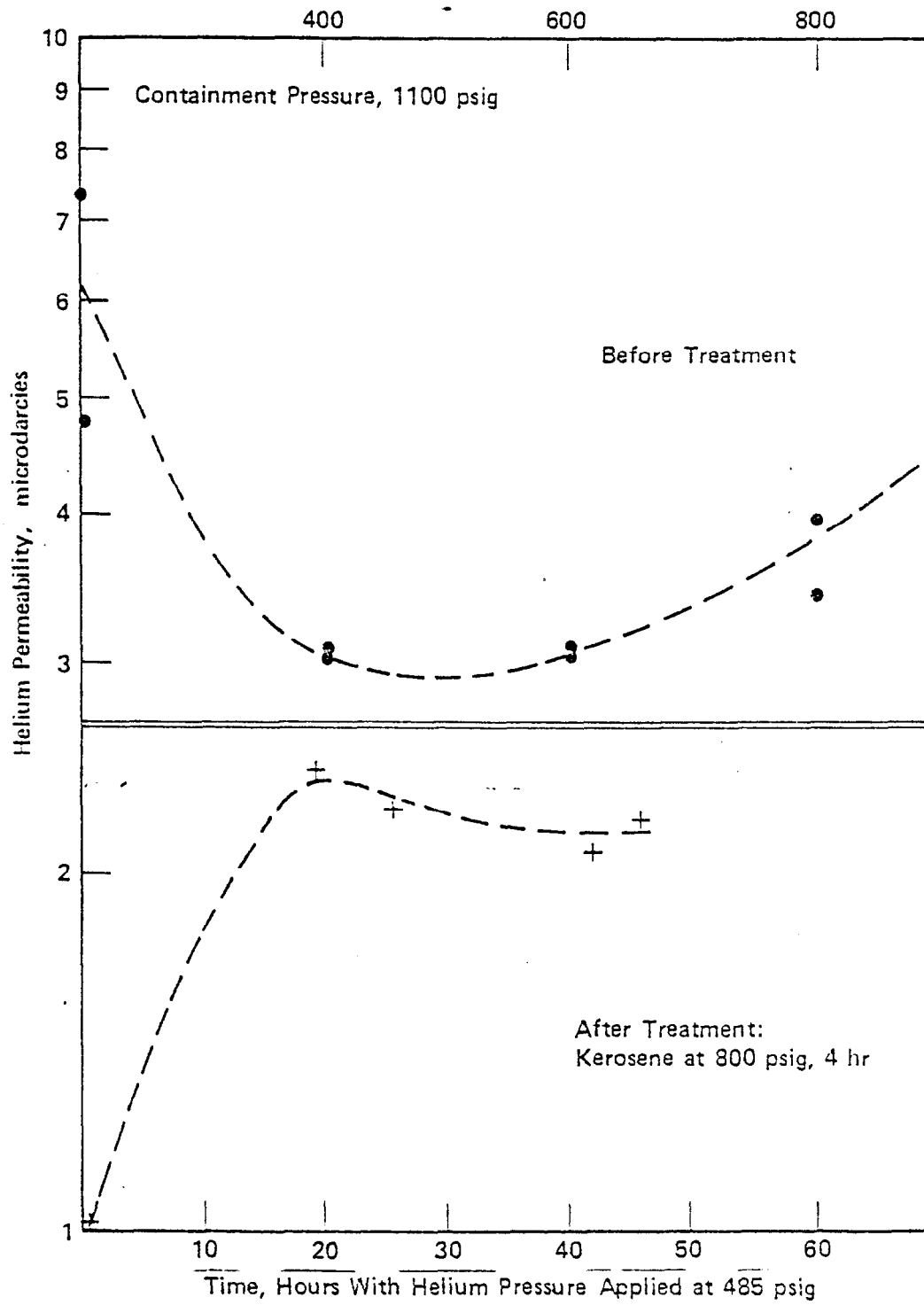


FIGURE 12.
HELIUM PERMEABILITY FOR SHALE SPECIMEN 20149-1030.32-a-4

Specimen 20149-680.14-b-4- Data on the specimen treated for four hours at 500 psig with foam fluid, which are presented in Figures 13 and 14, show that the permeability under 500 psig driving force was decreased from about 500 microdarcy to about 30 microdarcy initially. Flow recovered with time (Figure 14), but levelled off at about 40 percent of the initial rate. Permeability as a function of applied pressure (Figure 13) also is somewhat lower following the foam-fluid treatment.

Summary Discussion of Permeability/Treatment Investigation

In general, permeabilities have been observed in the ranges, zero to several hundred microdarcies at low (e.g., 200 psig) applied pressures, and zero to several thousand microdarcies at the high (e.g., 600 to 900 psig) applied pressures. Of immediate practical concern are the permeabilities at applied pressures near those of expected formation gas pressures, both before and after contact with the well-treatment fluids. Some data of this type have been assembled in Table 4, using 500 psig applied pressure.

Before treatment, permeabilities are seen to be generally in the ten to one hundred microdarcies range except for a high permeability (225 to 250 microdarcies) layer in the 680-foot core from Well 20149 and the low permeabilities (zero to six microdarcies) for specimens from the 1030-foot depth of that well.

Following treatment with fluid under pressure, the permeabilities are generally lower -- by one or two orders of magnitude in some cases. In these cases, this appears to be due to fluid blockage which clears under prolonged gas pressure and flow. In other cases, some type of blockage is seen to persist for long periods. The results for Specimen Oh 3-1015.5-a-3 again show that such persistent blockage sometimes can be cleared rapidly by use of vacuum.

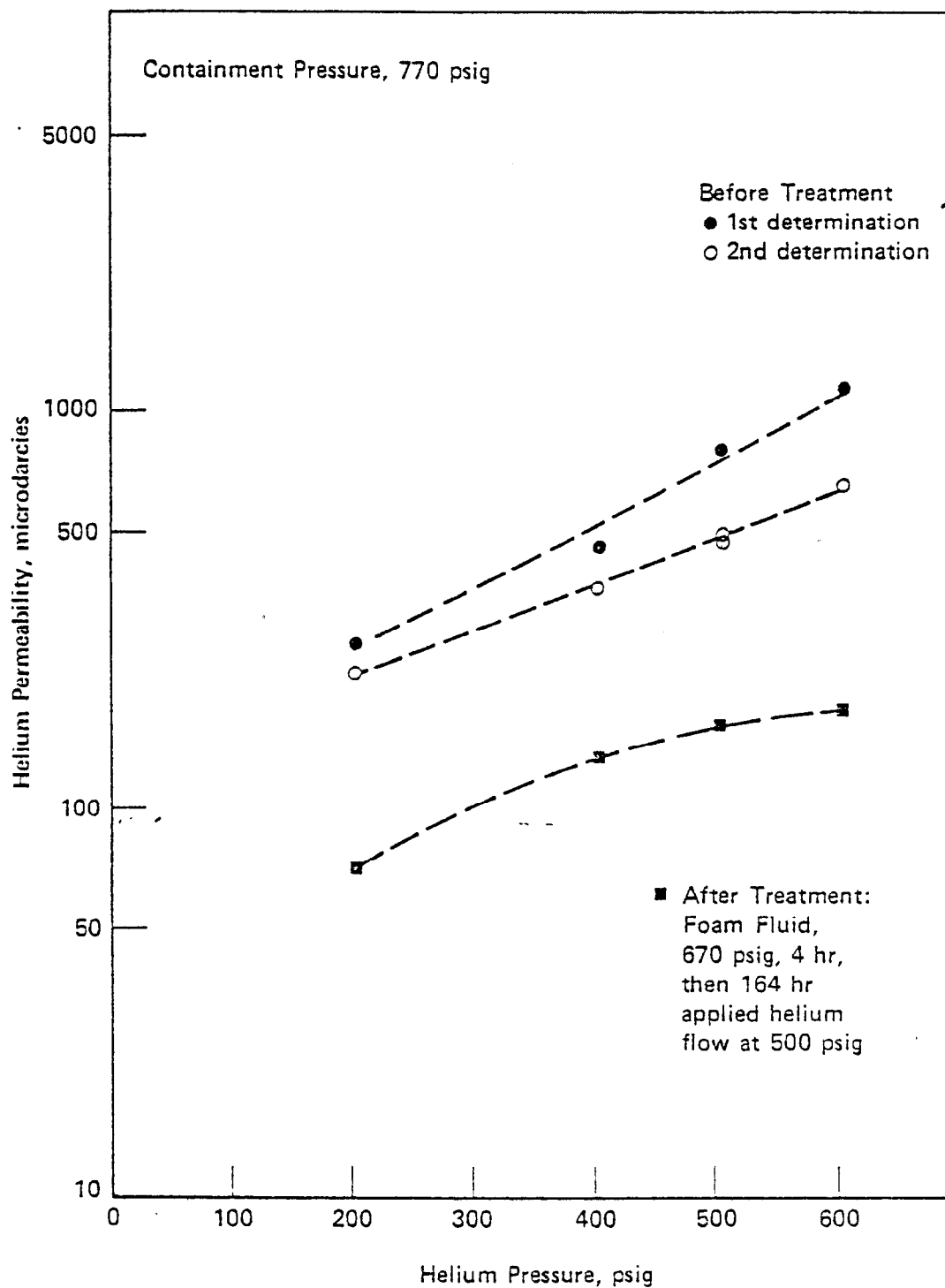


FIGURE 13.
HELIUM PERMEABILITIES FOR SHALE SPECIMEN 20149-680.14-b-4

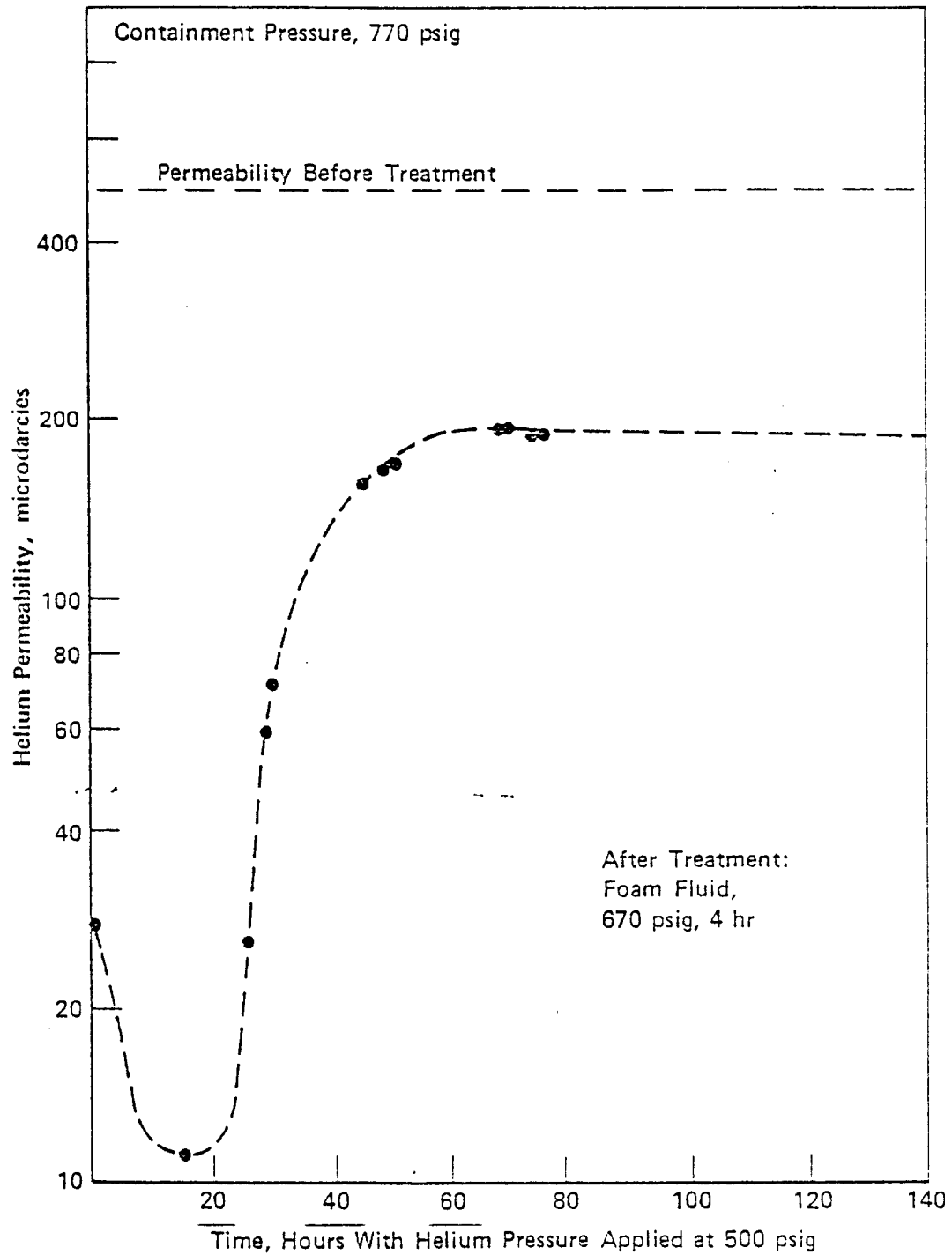


FIGURE 14.
RECOVERY OF PERMEABILITY WITH TIME FOR SHALE
SPECIMEN 20149-680.14-b-4 — AFTER FOAM-FLUID TREATMENT

TABLE 4.
SUMMARY OF PERMEABILITY DETERMINATIONS
(500 psig applied pressure)^(a)

Specimen	Flow Direction	Permeability Before Treatment, μ darcy	Permeability After Treatment, μ darcy	Treatment
20149-680.14-a-4	R	72		
-a-2	R	41	23 $\xrightarrow{172 \text{ hr}}$ 39	33% CO ₂ , 25 min, 680 psig
	F	13	33	
	R	--	35 $\xrightarrow{46 \text{ hr}}$ 36	33% CO ₂ , 25 hr, 670 psig
c-2	R	76, 93		
	F	58		
-b-2	F	225	3.3 $\xrightarrow{213 \text{ hr}}$ 9.3	33% CO ₂ , 64 hr, 670 psig
	R	256		
20149-1030.32-a-2	F	0 ^(b)		
	F	0 ^(c)		
-a-3	F	4.8, 6.1	2.5 $\xrightarrow{90 \text{ hr}^{(d)}}$ 0.9	33% CO ₂ , 4 hr, 800 psig
-a-4	F	3.1	--	
Oh 3-1015.5-a-1	F	17		
-a-2	F	11	9 $\xrightarrow{114 \text{ hr}}$ 9.7	
-a-3	F	64, 51 ^(b)	5.9 $\xrightarrow{165 \text{ hr}^{(e)}}$ 6.8	
	F		266 ^(e)	After 96 hr in vacuo

(a) Exceptions noted

(b) Polished specimen ends

(c) Scraped specimen ends

(d) 475 psig applied pressure

(e) 466 psig applied pressure

Evaluation of Effects by Other Methods

Work on other methods of evaluating the effects on the shale of treatment fluids is just getting underway. Methods that are being utilized include X-ray diffraction analysis, X-ray fluorescence analysis, scanning electron microscopy and electron probe analysis. Some emphasis is being placed on determination of the depth of penetration of the fluid as well as the nature of the effect.

SUMMARY

Experimental results have been presented which indicate that the shale is attacked by aqueous CO₂, supercritical CO₂ fluid and water at down-hole temperatures and at pressures equal to, or below, static pressures that might be used for fluid facing of the shale formations -- producing fractures and/or increase in permeability to gas flow in both short- and long-term treatment periods...

Data presented indicate that the effects of treatments with the fluids can be detected by permeability, ultrasonic-velocity-transmission and by visual observation.

Results of analyses of dissolved solids show that water primarily dissolved alkali constituents from the shale, whereas aqueous CO₂ dissolved primarily alkaline-earth and iron-containing species and was indicated to dissolve a greater proportion of the shale than the water did.

A test matrix designed to evaluate the degree of potential water blockage (formation damage) and the effect of vacuum drying as opposed to air drying gave inconclusive results, primarily because of the heterogeneity of the shale.

A unique facility has been developed in which the permeability of shale can be determined, the shale can be treated with well-completion fluids under simulated field conditions, then permeability can be remeasured -- without disturbing (and thus possibly altering) the shale specimen throughout the sequence. In this apparatus, shale permeability can be determined under applied confining pressures to simulate lithostatic pressure, with various median pressures, pressure differentials and gases (e.g., He, CH₄, H₂ and CO₂).

The first data available on the permeability of Devonian shale under simulated down-hole conditions have been generated.

Initial results of work directed toward investigation of the physical and chemical skin effects of hydraulic treatments of Devonian shale tend to confirm that fluid blockage occurs which, in some cases, has been observed to clear under prolonged gas pressure and flow. In other cases, however, blockage persists and it is not yet clear whether irreversible damage results.

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